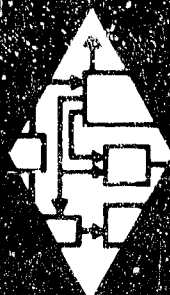


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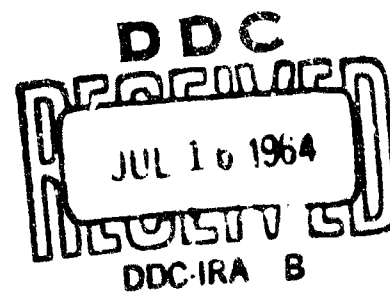


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A SURVEY OF FUELS  
SUITABLE FOR EXTERNAL  
COMBUSTION APPLICATIONS  
-----

TECHNICAL MEMO NO. 109

by

W. CHINITZ

A PROJECT DEFENDER RESEARCH STUDY

sponsored by

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prepared by

General Applied Science Laboratories, Inc.  
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Antonio Ferri  
President

June 1964

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LIST OF SYMBOLS

$a$	velocity of sound
$\Delta H_c$	heat of combustion
$\Delta H_v$	heat of vaporization
$h$	altitude
$M$	Mach number
$p$	pressure
$T$	Temperature
$V$	velocity
$\rho$	density

Subscripts

$c$	conditions on the cone surface
$o$	stagnation conditions
$\infty$	free-stream flight conditions

FORE WORD

This research was supported by the Advanced Research Projects Agency (Ballistic Missile Defense Engineering Office) as part of Project DEFENDER, under the technical direction of Mr. V. S. Kupelian, and was monitored by the U. S. Army Missile Command under Contract Number DA-30-069eAMC-216 (Z).

## SUMMARY

A wide variety of fuels are examined to determine those suitable for an external combustion application in a specified range of flight conditions. The original list of 27 fuels in 5 classes is reduced to 9 which are potentially acceptable. The 5 classes of fuels examined are: hydrocarbon and alcohol liquids, hydrocarbon gases, hydronitrogens, pyrophoric fuels and monopropellants. The nine selected fuels are: JP-4, JP-5, acetylene, TEA, TMA, TEB, TBB, pentaborane and aluminum borohydride. Further considerations regarding ignitability, stability of combustion and availability and cost indicate that only TEA, TMA, TEB and mixtures of hydrocarbons and these three pyrophoric fuels may be acceptable.

## I. INTRODUCTION

Recent developments in the control of hypersonic, atmospheric vehicles using combustion techniques (I. 1)\* and external burning lift-thrust devices (I. 2) require the use of fuels with unique properties. This stems from the adverse gas dynamic conditions under which the combustion must occur; for example, in many instances the free-stream flow is supersonic. As a result an ideal fuel would be one possessing all of the following properties:

1. Ease of storage. In this regard, fuels which are in the liquid phase at normal temperatures and pressures are preferable to those which are gaseous at these conditions and must be carried either at high pressure or cryogenically. High liquid fuel density is also desirable.
2. Ease and repeatability of ignition. It is clear that fuels which are pyrophoric under the flight conditions of interest possess an advantage over those which must be ignited by an external source; for example, spark ignition.
3. Low ignition delay and chemical reaction times.
4. High energy content.
5. Wide limits of inflammability.
6. Low heat of vaporization permitting rapid flashing of the liquid fuel into vapor.
7. A high degree of flame stability and good efficiency of combustion.
8. A ready availability and reasonably low cost.

---

\*Numbers in parentheses refer to references at the end of the report.



Clearly, no single fuel possesses all of the above characteristics and, as a result, the fuel(s) must be chosen on the basis of a specific mission requirement and must incorporate all the properties necessary to successfully carry out the mission. In Section II, a particular flight requirement is set forth and a number of potential fuels are evaluated in Section III. On the basis of the criteria outlined above, nine possible fuels are selected and their properties are discussed in Section IV.

## II. FLIGHT CONDITIONS

As an example of flight conditions involving the use of external combustion for hypersonic vehicle control, the following conditions are assumed:

Burning is desired on the surface of an  $8^\circ$  half-angle cone travelling in the velocity range of

$$6,000 \leq V_\infty \leq 10,000 \text{ ft./sec.}$$

in the altitude range of

$$3,000 \leq h \leq 20,000 \text{ ft.}$$

Under these altitude conditions, Reference (I. 3) indicates the following ranges of static temperature, pressure and density and velocity of sound:

$$508.0 \leq T_\infty \leq 447.4^\circ\text{R}$$

$$1896.6 \leq p_\infty \leq 972.49 \text{ lb/ft}^2$$

$$0.06998 \leq \rho_\infty \leq 0.04075 \text{ lb/ft}^3$$

$$1105.3 \leq a_\infty \leq 1037.3 \text{ ft/sec}$$

Using the data presented in Reference (I. 4) for supersonic flow over cones, the following ranges may be readily evaluated for conditions on the cone surface:

$$14.14 \leq p_c \leq 48.10 \text{ psia}$$

$$135 \leq T_c \leq 350^\circ\text{F}$$

$$2990 \leq T_{Oc} \leq 8350^\circ\text{F}$$

$$4.7 \leq M_c \leq 7.5$$

$$5850 \leq V_c \leq 9850 \text{ ft/sec}$$

It should be pointed out here that the temperatures throughout much of the boundary layer may be substantially higher than the inviscid static temperatures indicated above. The importance of this fact with regard to ignition of the fuel-air mixture is apparent.

### III. FUEL SELECTION

In Table I, a large number of fuels are tabulated along with several relevant properties of these fuels obtained from References II. 1-7, III. 1-5 and IV. 1-2. The fuels chosen for initial examination fall into five general categories:

Class 1. Hydrocarbon and Alcohol Liquids

Class 2. Hydrocarbon Gases

Class 3. Hydronitrogens

Class 4. Pyrophoric Fuels

Class 5. Monopropellants

In an effort to select fuels which might reasonably fulfill the external burning requirement set forth in the previous section, the following parameters were selected for examination:

1. Normal boiling point. When this parameter falls in the range of room temperature and above, the fuel may be readily stored and carried in the liquid state. All the class 1 fuels have boiling points in this range (Methyl alcohol is marginal) as do hydrazine (Class 3,) the Class 4 fuels, and the Class 5 fuels (hydrogen peroxide is also marginal). The remaining fuels must be stored under pressure and/or under refrigeration. It should be noted here that hydrogen has been omitted from consideration entirely because of its extremely low N. B. P. ( $-422.9^{\circ}\text{F}$ ), necessitating difficult and weighty cryogenic storage.

2. Liquid density. Due to space (volume) limitations, a high liquid density is desirable. Conversely, for a given volume allotment, a high liquid density permits the carrying of additional fuel. An examination of Table I indicates that butane, heptane, hexane, octane, the Class 2 fuels, ammonia, TEB, pentaborane, and aluminum borohydride possess relatively low liquid densities (less than, say, 45 lb./ft.<sup>3</sup>).

3. Heat of vaporization. As pointed out in Section I, for an external burning application, rapid flashing of the liquid fuel to the vapor phase is desirable. From Table I, it may be seen that most of the fuels have a fairly low  $\Delta H_v$  (say, less than 200 BTU/lb.) with the exception of acetone, ethane, ethylene, pentaborane and nitromethane, which are marginally poor, and the following which have substantially higher heats of vaporization: ethyl alcohol, methyl alcohol, the hydronitrogens and hydrogen peroxide.

4. Heat of combustion. This serves as a measure of the thermal energy which can ultimately be extracted from one pound of fuel. As such, a high value is always desirable. In this case, acetone, ethyl alcohol, methyl alcohol, the hydronitrogens and especially the monopropellants are inferior. Pentaborane and aluminum borohydride have particularly high values of  $\Delta H_c$ .

5. Limits of inflammability. For any combustion application, wide inflammability limits are desirable. Table I indicates values for this parameter in air at standard initial conditions. An outstanding fuel in this regard is acetylene, whose limits exceed even those of hydrogen (4.1-74% by volume).

The Class 4 fuels, by their pyrophoric nature, will react with almost any quantity of oxygen present. (Pentaborane appears to be somewhat restricted in this regard.) Hydrazine possesses exceptionally wide limits also.

6. Spontaneous ignition temperature. It is clear that a low value of this parameter circumvents the difficulties which carrying an ignition source engenders. By definition, the pyrophoric fuels have very low ignition temperatures, especially TEA, TMA and aluminum borohydride. Recalling that

$$135 \leq T_c \leq 350 \text{ }^{\circ}\text{F}$$

and that boundary layer temperatures will be somewhat higher, it may be seen that the following fuels might also prove satisfactory at the conditions of interest: heptane, hexane, pentane, octane, JP-4, JP-5, acetylene and hydrazine.

Using the above criteria, the following fuels are judged to be satisfactory for the specified application:

Class 1. JP-4 and JP-5 which possess reasonably high liquid densities, low  $\Delta H_v$ , average  $\Delta H_c$  and limits of inflammability, and low ignition temperature.

Class 2. Acetylene, which in spite of the necessity of carrying it under pressure (or at low temperature), must be considered by virtue of its very wide flammability limits and reasonably low spontaneous ignition temperature.

Class 3. Both fuels are precluded from use as a result of their low heats of combustion and high heats of vaporization.

Class 4. All six fuels tabulated in this category are acceptable for use on the basis of this initial evaluation.

Class 5. Very low heats of combustion, and a high  $\Delta H_V$  in the case of hydrogen peroxide, eliminate the fuels in this class from further consideration.

In the next section, a closer examination is made of the nine fuels selected above.

#### IV. PROPERTIES OF SUITABLE FUELS

The nine fuels selected for further evaluation are JP-4, JP-5, acetylene and the pyrophoric fuels: TEA, TMA, TBB, pentaborane and aluminum borohydride. In this section, a closer evaluation is made of the physical and thermochemical properties of these fuels, as well as a discussion of availability and cost.

##### A. Physical Properties

Curves of vapor pressure as a function of temperature are shown in Figure 1. An examination of the acetylene curve indicates that at room temperatures, pressures in excess of 700 psia will be required in order to carry this fuel in the liquid phase. Alternatively, if liquid acetylene is carried under its own vapor pressure at, say 50 psia, a temperature of about  $-85^{\circ}\text{F}$  is required. The remaining fuels are readily carried as liquids. In the cases of TEA, TBB and JP-5, fairly high temperatures are necessary to ensure flashing into the vapor phase. For example, at a pressure of 30 psia (which is in the range of the cone pressures), TEA requires a temperature of about  $400^{\circ}\text{F}$ , TBB about  $450^{\circ}\text{F}$  and JP-5 about  $470^{\circ}\text{F}$  to bring about a phase change. In applications where flashing to the vapor phase is desirable to promote stable combustion, these fuels may prove unsatisfactory.

On the other hand, these three fuels possess higher liquid densities than the others, as shown in Figure 2. TEB, pentaborane, and aluminum borohydride have somewhat lower liquid densities, particularly the last-named.



Clearly a more specific mission requirement is necessary in order to reach a decision on the minimum acceptable liquid density.

Other physical properties of these fuels of less immediate interest (e. g., surface tension, viscosity, etc.) are readily obtainable from the cited references.

#### B. Thermochemical Properties

With the exception of pentaborane and aluminum borohydride, the fuels chosen have heats of combustion in the hydrocarbon range of 18,000 - 20,000 BTU/lb. (see Table I). Pentaborane has the highest  $\Delta H_c$  (29,100 BTU/lb.), which may make it preferable for applications in which particularly high temperatures or velocities are desirable. However, its range of pyrophoricity is restricted (Figure 3). No data is available on its ignition delay or chemical reaction times. In addition, there are limitations on pentaborane's cost and availability, as will be discussed subsequently.

Aluminum borohydride also possesses a somewhat higher heat of combustion (24,800 BTU/lb.). It is, in addition, very highly reactive when compared with other pyrophoric fuels. For example, in Reference I. 5 it is shown that at the adverse tunnel conditions of Mach 2 flow (2.8 psia, 312°R), aluminum borohydride and hydrocarbon-aluminum borohydride mixtures (22% and 41% by weight of JP-4) ignited easily on the tunnel wall (pentaborane ignited with less ease), whereas TMA, TMB, TEB and other pyrophoric fuels tested either failed to ignite or burned in the tunnel diffuser. A severe restriction

to the use of aluminum borohydride, however, lies in its lack of availability and inordinately high cost, as will be discussed presently.

The remaining pyrophoric fuels are similar in characteristics except for the somewhat high spontaneous ignition temperature of TBB (190°F). Their small ignition delay times when compared with the JP fuels and acetylene are demonstrated in Figures 4 and 5. It should be pointed out that all the pyrophoric fuels possess the disadvantage of creating solid constituents as a product of combustion. For the case of the aluminum-containing fuels, this product is aluminum oxide ( $Al_2O_3$ ) and for the boron compounds, it is boric oxide ( $B_2O_3$ ). The detrimental effect of these solid constituents generally takes the form of plugged valves, pipes and injectors unless extreme care is taken. Even then the problem may be unavoidable. Here again, a further definition of the overall mission requirement and equipment is necessary prior to reaching a decision on the use of these fuels.

For the problem at hand, the JP fuels or acetylene might prove adequate. In the event that the elevated boundary layer temperatures are insufficient to ignite these fuels, external ignition will be required (spark igniter, hot wire, etc.). In the experiments of Reference 1.5, a 59% JP-4 (by weight)-aluminum borohydride mixture could not be successfully ignited in the desired region, resulting in a weak flame downstream of the spark plug used in these experiments. Also, it was shown that tandem injection of JP-4 and aluminum borohydride resulted in burning only when the latter was present. The JP-4 was unable to sustain combustion by itself.

It appears, then, that for most external burning applications in supersonic

flows one of the pyrophoric fuels must be used, although mixtures of hydrocarbons and pyrophorics may also be possible fuels.

### C. Availability and Cost

No consideration will be given here to the hydrocarbon fuels which are readily available. Of the pyrophoric fuels, pentaborane and aluminum borohydride are by far the most expensive and most difficult to obtain. For example, a discussion with the Fuel and Propellant Product Manager at the Callery Chemical Company revealed that they no longer manufacture pentaborane on a production scale. Laboratory preparation of this fuel escalates the cost to about \$450 per pound.

However, a large supply of pentaborane exists in inventory (about  $2 \times 10^5$  pounds) at a former Callery production site in Oklahoma. Permission to obtain the fuel from this source must be obtained from the Air Force, and the price is of the order of \$15 per pound.

A similar situation exists with aluminum borohydride. A former manufacturer of this compound (Metal Hydrides, Inc., Beverly, Mass.) no longer produces the fuel except on a small laboratory scale. Under these circumstances the cost is of the order of \$50,000 for the initial two pound batch

On the other hand, the remaining pyrophoric fuels are readily available at far lower cost from such firms as Texas Alkyls and the Ethyl Corp. For example, in 32 pound cylinders a recent Texas Alkyl Price Schedule (2/18/63) indicates the cost of TEA as \$2.15 per pound. In very large quantities (i.e., 30,000 lbs. or greater), the price drops to \$1.50 per pound. Equivalent prices hold for the other pyrophoric fuels.

From the above, it may be concluded that unless full scale production of pentaborane or aluminum borohydride is resumed, one of the more readily available pyrophoric fuels must be employed.

## V. CONCLUSIONS

A survey has been made of a large number of fuels in an effort to determine the most suitable for use in a specified external burning application. The original list of 27 fuels in five classes is reduced, after a preliminary evaluation, to nine acceptable fuels: JP-4, JP-5, acetylene, TEA, TMA, TEB, TBB, pentaborane and aluminum borohydride. The latter six of these fall into the class of pyrophoric fuels. Mixtures of JP and pyrophorics may also prove acceptable.

Additional limitations tend to reduce this list still further. For example, under the flight conditions of interest, spontaneous ignition of JP-4, JP-5 and acetylene is marginal. As a result, one of the pyrophorics must very likely be used.

At the lower condition of cone surface temperature (135°F) the high spontaneous ignition temperature of TBB (190°F) makes this fuel unacceptable. In addition, availability of pentaborane and aluminum borohydride is extremely restricted, and prices are very high.

As a result, for most missions carried out in the specified ranges of flight conditions, the three pyrophoric fuels, TEA, TMA, and TEB appear to be the most satisfactory.

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**TABLE I**  
**SOME PHYSICAL AND COMBUSTION PROPERTIES OF SELECTED FUELS**

FUEL	FORMULA	MOLECULAR WEIGHT	NORMAL BOILING POINT (°F)	LIQUID DENSITY AT 60°F (lb/ft <sup>3</sup> )	HEAT OF VAPORIZATION AT 60°F (Btu/lb)	HEAT OF COMBUSTION AT 77°F (Btu/lb)	LIMITS OF INFLAMMABILITY (% by vol.)	SPONTANEOUS IGNITION TEMP. (°F)
<b>CLASS 1 FUELS: HYDROCARBON AND ALCOHOL LIQUIDS</b>								
ACETONE	C <sub>3</sub> H <sub>6</sub> O	58	133.1	49.4	237	13,300	3-11	1042
BENZENE	C <sub>6</sub> H <sub>6</sub>	78	176.4	54.9	170	17,446	1.4-6.7	1076
BUTANE	C <sub>4</sub> H <sub>10</sub>	58	31.8	36.4	165.7	19,665	1.5-8.5	826
ETHYL ALCOHOL	C <sub>2</sub> H <sub>6</sub> O	46	173.0	49.6	367	11,930	3.5-19	738
HEPTANE	C <sub>7</sub> H <sub>16</sub>	100	209.2	42.7	137.4	19,314	1-6	451
HEXANE	C <sub>6</sub> H <sub>14</sub>	86	155.7	41.2	160.4	19,391	1.2-6	478
METHYL ALCOHOL	CH <sub>3</sub> OH	32	148.1	49.5	473	9,078	6.1-36.5	878
PENTANE	C <sub>5</sub> H <sub>12</sub>	72	96.8	39.1	153.8	19,499	1.3-6	527
OCTANE	C <sub>8</sub> H <sub>18</sub>	114	257	43.9	128	19,197	0.95-3.20	446
TOLUENE	C <sub>7</sub> H <sub>8</sub>	92	231.8	54.0	156	18,300	1-6	1026
JP-4	C <sub>n</sub> H <sub>2n</sub>	83	218	46.9*	138	18,400*	0.8-5.63	484
JP-5	C <sub>n</sub> H <sub>2n</sub>	146	400	49.1*	120	18,300*	0.6-4.53	475*
<b>CLASS 2 FUELS: HYDROCARBON GASES</b>								
ACETYLENE	C <sub>2</sub> H <sub>2</sub>	26	-119	38.4	356.0	20,776	2.5-82	581
ETHANE	C <sub>2</sub> H <sub>6</sub>	30	-127.7	23.4	232.2	20,432	3.2-12.5	882
ETHYLENE	C <sub>2</sub> H <sub>4</sub>	28	-155	35.4	213.3	20,295	3.0-29.0	914
PROPANE	C <sub>3</sub> H <sub>8</sub>	44	-42.7	31.8	183.28	19,944	2.4-9.5	898
PROPYLENE	C <sub>3</sub> H <sub>6</sub>	42	-54	32.6	195.4	19,691	2.0-9.7	856
<b>CLASS 3 FUELS: HYDROGENS</b>								
AMMONIA	NH <sub>3</sub>	17	-28	37.2	588	8,001	16-27	1204
HYDRAZINE	N <sub>2</sub> H <sub>4</sub>	32	236	62.4	550	7,770	47-100 <sup>++</sup>	104
<b>CLASS 4 FUELS: PYROPHORIC FUELS</b>								
TEA	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Al	114	367	52.0	130	18,300	—	LESS THAN FREEZE PT.
TMA	(CH <sub>3</sub> ) <sub>3</sub> Al	72	255	46.4	120	17,820	—	LESS THAN FREEZE PT.
TEB	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> B	98	203	42.6	161.6	20,230	—	-4
TBB	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> B	102	410	49.4	136.5	19,500	—	190
PENTA-BORANE	B <sub>5</sub> H <sub>9</sub>	63	140	39.2	208	29,130	14-27 <sup>+</sup>	670
ALUMINUM HYDRIDE	AlH <sub>3</sub>	71.5	113	34.6	181.2	24,800	—	LESS THAN FREEZE PT.

\* MINIMUM

\* AT 1 ATM (LIMITS OF SPONTANEOUS INFLAMMABILITY)

\*\* AVERAGE

++ EXPLOSION LIMITS AT 1 ATM.

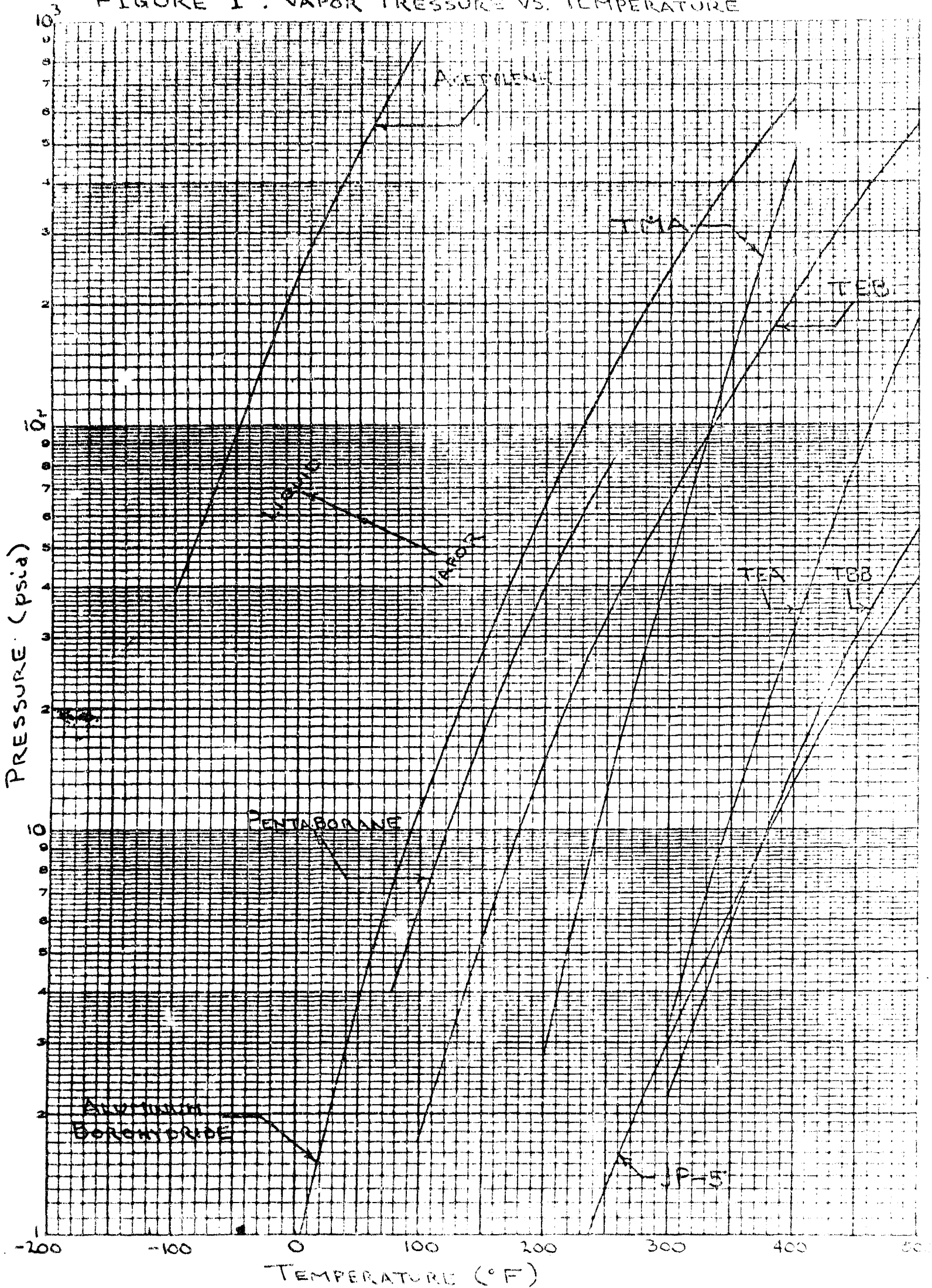
FUEL	FORMULA	MOLECULAR WEIGHT	NORMAL BOILING POINT (°F)	LIQUID DENSITY AT 60°F (lb/ft³)	HEAT OF VAPORIZATION (Btu/lb)		HEAT OF COMBUSTION (Btu/lb)		LIMITS OF FLAMMABILITY (% BY VOL)	SPONTANEOUS IGNITION TEMP. (°F)
					AT 77°F	AT 77°F	AT 77°F	AT 77°F		
CLASS 3 FUELS: MONOPROPELLANTS										
HYDROGEN PEROXIDE	H <sub>2</sub> O <sub>2</sub>	34	312	90.5	540	1335 <sup>++</sup>	—	—	—	—
NITRO-METHANE	CH <sub>3</sub> NO <sub>2</sub>	61	214	70.6	242	1956 <sup>✓</sup>	—	—	—	—
						4800 <sup>✓</sup>	—	—	—	—

<sup>++</sup> CATALYTIC DECOMPOSITION TO H<sub>2</sub>O +  $\frac{1}{2}$  O<sub>2</sub>

✓ AS A MONOPROPELLANT

✓ AS A FUEL WITH AIR

FIGURE 1. VAPOR PRESSURE VS. TEMPERATURE



ENGINEERING CORPORATION  
MADE IN U. S. A.

NO. 1311  
TZOE APH R  
SEMI-LOGARITHMIC  
3 CYCLES X 10 DIVISIONS PER INCH

FIGURE 2. FUEL DENSITIES AS A FUNCTION OF TEMPERATURE

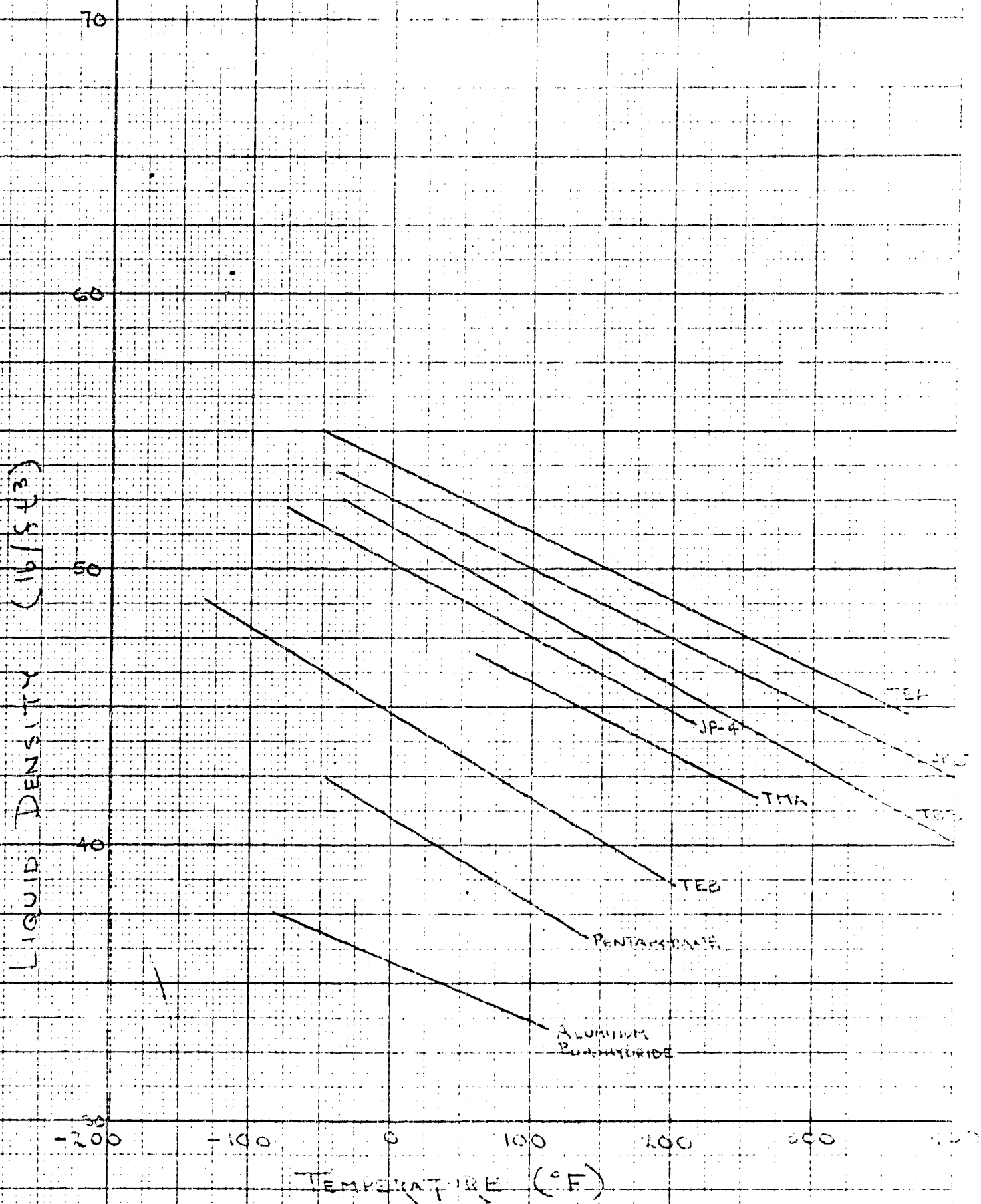


FIGURE 3

